

1/PRTS

METHOD AND DEVICE FOR PRODUCING SHAPED CERAMIC BODIES
USING SETTER PLATES

Background Information

The present invention is based on a method and a corresponding device for producing shaped ceramic bodies according to the species defined in the generic claims.

Such a method is described, for example, in the German Patent 43 09 005 A1 in which a method was introduced for producing multilayer hybrids from a plurality of ceramic green sheets which contain organic auxiliary agents as binders and sintering aids, and which are provided with printed circuit traces and plated-through holes. The stack of green sheets is pressed together by two porous, ceramic setter plates during sintering and removal of the binder, to ensure the least possible shrinkage and buckling within the green sheets. To achieve a simple separation between the setter plates and the multilayer hybrid after the sintering process, the setter plates were furthermore provided with a porous separating layer made, for example, of aluminum oxide which can be applied by slip casting or silk-screen printing. The organic auxiliary agents in the form of the binder or sintering additive are largely pyrolyzed during the binder removal or sintering, for example, in a hot press under axial pressure, and escape as organic bake-out products. In this context, the escape takes place, inter alia, via the porous setter plates or the applied porous separating layers which are gas-permeable. Damage to the ceramic sheets due to burning out

the organic auxiliary agents too quickly, the diffusion of the broken-up, split-off or partially-burned organic bake-out products through the setter plates, and the maximum portion of hydrocarbons in the oven atmosphere in order to remain below the explosion limiting values are determinant of the speed for the duration of the binder removal and sintering process.

The object of the present invention is to further develop the existing method in such a way that the necessary period of time for the sintering and removal of binder from the shaped ceramic bodies is markedly shortened without, for example, exceeding the explosion limiting values in the oven atmosphere.

Advantages of the Invention

Compared to the related art, the method of the present invention, having the characterizing features of the generic claims, has the advantage that, by introducing a catalytically active substance into the pores of the porous setter plates and/or into the pores of the porous separating layers, a catalytic conversion of the gaseous bake-out products, escaping when baking out the green bodies, is at least partially achieved. The bake-out products are, in particular, decomposition products of the organic auxiliary agents and contain hydrocarbons, among other things.

The escaping bake-out products are preferably converted into less combustible or incombustible gases, so that the method of the present invention makes it possible to bake out more organic auxiliary agents per unit of time than previously, without, for example, the explosion limiting values for hydrocarbons being reached in the oven atmosphere. This

results in a considerable time savings during the sintering and/or removal of the binder from the green bodies, and thus to a shortening of the oven cycles, which means a marked cost reduction and a substantially lower need for investment in oven installations.

Moreover, catalytically converted, low-molecular oxidation or bake-out products diffuse more quickly through the porous setter plates and the optionally provided separating layers, than unconverted, high-molecular bake-out products, which means a further time savings during production. Incidentally, installations, existing owing to the method of the present invention, for the catalytic afterburning of the waste gases carried away from the ceramic green bodies via the setter plates can be designed to be smaller.

In addition to being introduced into the porous setter plates, the catalytically active substance can also be introduced into the porous separating layers, which brings with it advantages from the standpoint of process engineering. In addition, given an appropriate activity of the introduced, catalytically active substance, in some cases it is even sufficient if the substance is only in the porous separating layers, which leads to a markedly reduced need for these sometimes expensive materials. In the same way, for some purposes it can be sufficient if the catalytically active substance is merely introduced into the surface area of the porous setter plates or separating layers, for example, by spraying on or impregnating. This also reduces material costs.

More advantages and advantageous further developments of the present invention are apparent from the measures indicated in the subclaims.

Thus, one particularly advantageous refinement of the method according to the present invention uses starting materials which, at the latest in the course of a thermal aftertreatment of the setter plates and the separating layers, respectively, are converted to form metallic, nano-scale particles and are located in the pores of the setter plates and/or the separating layers.

Also very advantageous is the selection of a metallic-salt solution as starting material for introducing the catalytically active substance, in the case of which no unwanted, in particular inorganic residues remain in the setter plates or separating layers after the thermal aftertreatment.

For faster removal of gaseous bake-out and conversion products, the setter plates can advantageously be provided with additional gas outlets arranged, in particular, parallel to the surface of the setter plates.

Drawing

The single Figure shows a diagrammatic sketch of a ceramic multilayer hybrid composed of a stack of ceramic sheets between two porous setter plates which are separated from the stack of sheets by porous separating layers.

Exemplary Embodiments

Exemplary embodiments of the present invention are explained more precisely in the following with reference to the Figure. A shaped ceramic body, which, for example, can be one ceramic sheet, a stack of ceramic sheets or a ceramic multilayer

hybrid 10 composed of ceramic sheets 1, 2, 3, 4, 5, that is provided with printed circuit traces, switching elements and plated-through holes (not shown in the Figure), is situated between two porous setter plates 20, 21 which, on the surface on the side facing multilayer hybrid 10, are provided with porous separating layers 30, 31. Setter plates 20, 21 are provided with gas outlets 22, e.g. in the form of channels running parallel to the surface of the plates, for more rapid removal of escaping gases. The shaped ceramic body, that is to say, multilayer hybrid 10, exists initially as a green body and, in addition to ceramic components, also contains organic auxiliary agents, e.g. in the form of binders, sintering additives, softeners and residues of solvents.

Setter plates 20, 21 are made of porous, ceramic materials and are gas-permeable for organic bake-out products which develop during binder removal and/or sintering of the shaped ceramic bodies. They are preferably gas-permeable for low-molecular, gaseous oxidation products such as CO, CO₂, H₂O, CH₄, as well as simple hydrocarbons.

The process of sintering and/or removing binder from multilayer hybrid 10 is carried out in a hot press under axial pressure, setter plates 20, 21 in particular preventing sintering shrinkage of multilayer hybrid 10 from occurring in the plane of setter plates 20, 21. Since, because of their fragility, it is very difficult to handle multilayer hybrids 10 from which the binder has been removed, the entire binder removal and sintering process must be carried out in the hot press, although typically less than one hour of 11.5 hr. of firing time is necessary for the actual sintering under pressure. Essentially the removal of binder from multilayer hybrid 10 by gradual bake-out is carried out during the

remaining time, as a result of which the organic auxiliary agents are thermally decomposed to a great extent, or volatilize, undecomposed, from the green body and are carried away to the outside through the gas-permeable setter plates.

5 Thus, essentially the time for the diffusion of the cracked or partially-burned, organic constituents through setter plates 20, 21 is speed-determinate for the binder removal process. Since the organic constituents contain a high portion of hydrocarbon compounds, for reasons of operational safety
10 (protection against explosion), the binder removal process must be carried out in such a way that the concentration of hydrocarbons in the oven atmosphere always remains below the explosion limiting values.

15 Porous separating layers 30, 31 simplify the removal of ready-sintered multilayer hybrid 10 from setter plates 20, 21. For example, the separating layers contain essentially ceramic constituents such as aluminum oxide and are preferably applied on setter plates 20, 21 by silk-screen printing or slip
20 casting. However, the method of the present invention can also be implemented without separating layers 30, 31. Porous separating layers 30, 31, like setter plates 20, 21, are gas-permeable for organic bake-out products from the ceramic green body.

25 The essence of the present invention is the introduction of a catalytically active substance into setter plates 20, 21 and/or separating layers 30, 31 prior to beginning the actual process of sintering and/or removal of binder from the shaped
30 ceramic bodies, in order to accelerate the implementation of this binder removal process.

Catalytically active noble metals such as palladium, rhodium

or platinum are suitable for this purpose. The specific selection of the catalytically active substance in the individual case is made according to the type of the organic auxiliary agents and their quantity, as well as the sintering or binder-removal temperatures utilized, it always being necessary to take into account the catalytic activity of the respective material and its costs. The catalytically active substance is used specifically to catalytically convert organic auxiliary agents escaping from the green body during sintering and/or binder removal. To that end, it is very advantageous if it is located in the pores of the porous materials of setter plates 20, 21 and/or of porous separating layers 30, 31, where it is easily available for the escaping gases and can develop a suitably high activity. The catalytically active substance catalytically converts the organic hydrocarbon compounds contained in the escaping bake-out products by, for example, oxidizing them or converting high-molecular, organic hydrocarbon compounds to form low-molecular hydrocarbon compounds. In particular, it is used for the oxidation of easily combustible hydrocarbons into incombustible or non-explosive compounds which are then removed via the pores in setter plates 20, 21 and/or separating layers 30, 31, as well as via gas outlets 22.

The catalytically active substance can be introduced into setter plates 20, 21 and separating layers 30, 31, respectively, by dipping setter plates 20, 21 into an appropriate metallic-salt solution, or by spraying the surface area of setter plates 20, 21 with this solution. In this context, setter plates 20, 21 can already have been provided with separating layers 30, 31 beforehand, so that the catalytically active substance is also introduced into separating layers 30, 31.

By dipping, the catalytically active substance is distributed essentially uniformly within setter plates 20, 21, and optionally within separating layers 30, 31, as well. By spraying in particular the side of the porous plates facing the ceramic green body, the catalytically active substance is present largely on the surface on setter plates 20, 21 and separating layers 30, 31, respectively. One skilled in the art must check in the individual case, on the basis of a few simple experiments, which method is the most suitable in each case. Spraying has the advantage that the quantity of catalytically active material used up is relatively small, which means lower material costs. On the other hand, because of the distribution on the surface, only a small part of the volume of setter plates 20, 21 is catalytically active, which means a correspondingly longer or more incomplete catalytic conversion of the organic bake-out products. However, since the catalytically active materials that are possible also differ with respect to their catalytic activity, one skilled in the art, through preliminary experiments, must find in the individual case an optimum between the material costs and the local distribution of the catalytically active substance, as well as the degree of the catalytic conversion and the time resulting for the binder removal.

In further exemplary embodiments, the catalytically active substance is introduced only into separating layers 30, 31, for example, by subsequent spraying, it again being necessary in the individual case to weigh advantages and disadvantages from the standpoint of process engineering against material costs and the time savings attained during the binder removal.

To ensure a homogenous and very fine distribution of the catalytically active substance in setter plates 20, 21 and

separating layers 30, 31, respectively, or in the corresponding surfaces, they are preferably steeped in an aqueous metallic-salt solution containing at least one of the metallic salts PtCl_6 , PdCl_2 , RhCl_3 , platinum acetate, rhodium acetate or palladium acetate. The concentration of the catalytically active substance in this metallic-salt solution is preferably between 0.1 g/l to 30 g/l. Concentrations of 1 g/l to 15 g/l have turned out to be particularly advantageous. In this case, in a setter plate 20 weighing 1 kg, when using a platinum solution containing 10 g of platinum to 1 liter of solution, approximately 0.6 g of platinum is introduced into setter plate 20. When using a solution containing 6 g of palladium to 1 liter of solution, approximately 0.4 g of palladium is introduced per plate.

After setter plates 20, 21 have been sprayed or dipped, a thermal aftertreatment of setter plates 20, 21 with the introduced catalytically active substance is expediently carried out. Depending on the size of the plates, the type of metal introduced and the metallic-salt solution employed, this aftertreatment lasts from 30 minutes to 5 hours at a temperature of 100°C to 700°C . It is preferably carried out in a gas atmosphere, such as air or nitrogen, which does not oxidize the catalytically active substance. However, when working with a few catalytically active materials which can be oxidized relatively easily, in order to avoid oxidation, it is best if work is carried out in a reductive gas atmosphere. For example, in the case of platinum, rhodium and palladium, it is sufficient if the thermal aftertreatment is carried out at 500°C over 2 hr. in air.

The use of organic metallic compounds, such as the acetates indicated, is particularly recommendable for applications in

which no residues of the introduced metallic-salt solution are to remain in setter plates 20, 21 and separating layers 30, 31 after the thermal aftertreatment, since these compounds thermally decompose in a substantially residue-free manner during the thermal aftertreatment.

It has turned out to be particularly advantageous if the catalytically active substance is present in the form of uniformly distributed, nano-scale, metallic colloids of, for example, platinum, rhodium or palladium in the pores of the porous setter plates and separating layers, respectively. The size of these colloids is advantageously between 3 nm and 100 nm, in order to attain the highest possible specific surface areas, and thus an effective seeding of setter plates 20, 21 or of separating layers 30, 31.